

<b>REPORT DOCUMENTATION PAGE</b>		Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 9/28/98	3. REPORT TYPE AND DATES COVERED Final	
4. TITLE AND SUBTITLE Molecular Interactions and Reaction Dynamics in Supercritical Water Oxidation		5. FUNDING NUMBERS DAAL03-92-G-0174	
6. AUTHOR(S) K.P. Johnston, M.A. Fox, and A.J. Bard		Subcontract under ARO Proposal 30346-CH-URI	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemical Engineering University of Texas at Austin Austin, TX 78712		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER  ARO 30374-1-CH-URI	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE  19990104 062	
13. ABSTRACT (Maximum 200 words)			

In this project we developed the use of novel techniques for addressing acid-base equilibria, chemical kinetics and related phenomena in high temperature water: UV-vis and fluorescence measurements of acid-base equilibria, fluorescence decay measurements of proton transfer reactions at the ns time frame, pulse radiolysis of reaction intermediates in organic reactions, and fully molecular computer simulation of ion solvation, acid base equilibria, and ion diffusion. We have shown that UV-vis spectroscopy is well-suited for measuring chemical equilibria in SCW. From UV-vis spectroscopic measurements and molecular dynamics simulation of chemical equilibria, we have shown that density effects on broad classes of reactions may be explained in terms of changes in charge dispersal between the relevant chemical states. With single photon counting and pulse radiolysis fast kinetics measurements, in-situ chemical dynamics of organic reactions has been studied. A relatively robust titanium reactor has been designed for studying electrochemical reactions in SCW.

14. SUBJECT TERMS Supercritical water, Solution Chemistry, Chemical dynamics, High temperature			15. NUMBER OF PAGES 19
			16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL

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## Statement of problem solved

Hydrothermal oxidation is an enclosed and complete treatment process for military wastes making it more attractive to the public than incineration. It has the potential to destroy a variety of military wastes including chemical warfare agents, energetic materials, and wastewater. Above water's critical temperature, 374°C, most organics, oxygen, and water mix fully leading to highly efficient oxidation, with the fuel value coming from the organics.

A major obstacle to development of hydrothermal technology has been a lack of scientific knowledge of the chemical kinetics and solution chemistry and thermodynamics in supercritical water (SCW). Because water at high temperatures is highly compressible, the density can vary over a large range with conditions, and the dielectric constant can range from 1.5 to 10; correspondingly, large variations in ion solvation and acid-base equilibria are expected. Consequently, changes in these properties will have a profound effect on the key issues in hydrothermal technology: waste destruction efficiency, salt solubility, metal-ion complexation, acid-base catalysis of hydrolysis and oxidation reactions, and reactor corrosion.

To achieve breakthroughs which could make hydrothermal oxidation a successful technology, our objective has been to develop a fundamental molecular understanding of the thermodynamics of ion solvation and acid-base equilibria in SCW and how it affects chemical kinetics. We have used this knowledge to develop easily implemented but molecular-based models. Knowledge of pH and the thermodynamic properties of acid-base reactions in SCW is crucial to understanding the thermochemistry and reaction chemistry of hydrothermal processes such as oxidation of organics, metal corrosion, formation and precipitation of metal-hydroxy complexes and/or salts, catalysis, and hydrolysis. Furthermore, we have addressed ionic transport behavior and corresponding simplified models for the correlation of transport coefficients with conditions and ionic character.

## Summary of Most Important Results

In this project we developed the use of novel techniques for addressing acid-base equilibria, chemical kinetics and related phenomena in high temperature water: UV-vis and fluorescence measurements of acid-base equilibria, fluorescence decay measurements of proton transfer reactions at the ns time frame, pulse radiolysis of reaction intermediates in organic reactions, and fully molecular computer simulation of ion solvation, acid base equilibria, and ion diffusion. We have shown that UV-vis spectroscopy is well-suited for measuring chemical equilibria in SCW. pH indicators were developed for the first time for in-situ measurements of the pH of unknown solutions and to perform acid-base titrations and develop neutralization strategies for hydrothermal oxidation. The reaction equilibria of Cr (VI) was measured in SCW, as it plays a key role in corrosion. We also determined the equilibria for  $\text{HNO}_3$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2$ ,  $\text{HNO}_2$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$  which play a key role in corrosion and salt management. We simulated free energies of reaction and ion solvation in SCW for the first time and related these results to the solution structure to provide a complete molecular description. From UV-vis spectroscopic measurements and molecular dynamics simulation of chemical equilibria, we have shown that density effects on broad classes of reactions may be explained in terms of changes in charge dispersal between the relevant chemical states.

With single photon counting fast kinetics measurements, it was found that proton transfer reactions from 2-naphthol to water and ammonia exhibit strong deviations from Arrhenius behavior at temperatures above 200°C due to changes in the structure of water. In contrast, proton transfer to anions exhibits Arrhenius behavior up to the critical point of water. In another type of fast kinetics study, pulse radiolysis techniques have been used as a route for activating organic solutes in SCW. In this technique, high energy electrons bombard a solution inducing ionization of solvent and, upon equilibration, solute. By electron attachment, the corresponding solute radical anions and their fragmentation products have been observed. The hydroxy radical is a primary

radiation product in water. Its subsequent chemical reactivity has been monitored by optical methods to understand how the structure of SCW influences reaction dynamics.

A relatively robust titanium reactor has been designed for studying electrochemical reactions in SCW. Glasses with high PbO content remain good electrical insulators at high temperature, and have thermal expansion coefficients that are close to that of most metals. Corrosion of these glasses is slow enough to be acceptable in many cases. Redox reactions have been studied for various inorganic and organic substances, and diffusion coefficients have been measured.

## 1. List of Manuscripts published or submitted Review paper

Keith P. Johnston, Peter J. Rossky, and Perla B. Balbuena, Solution chemistry in supercritical water: spectroscopy and simulation, NATO ASI Institute on Supercritical Fluids, Kemer, Turkey 1998, in preparation (1998).

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## 2. Scientific personnel

### *Personnel supported*

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### **Degrees**

Perla Balbuena, Ph.D., Gerald Bennett, Ph.D, Lewis Flanagan, M.S., Ram Gupta, Ph.D, Carson Meredith, Ph.D, Tim Rhodes, Ph.D, William Wofford, Ph.D., Tao Xiang, Ph.D.

### **3. Inventions- none**

## **4. Scientific Progress**

### **Absorbance spectroscopy of chemical equilibria in supercritical water with the use of pH indicators**

Spectroscopic techniques have been used to study solution chemistry and acid-base chemistry in SCW, particularly in the key temperature range from 320 to 420 °C where corrosion is often most severe.(Chlistunoff & Johnston, 1998; Johnston & Chlistunoff, 1998; Xiang & Johnston, 1997) These studies are highly relevant for understanding corrosion, catalysis, and salt solubilities in hydrothermal oxidation processes, key issues in the technology. Most previous studies of chemical equilibria above 350 °C were made with conductivity measurements and were limited to dissociation of a single neutral species to two ions, for example  $\text{HCl} = \text{H}^+ + \text{Cl}^-$ . In contrast, our spectroscopic measurements have been applied to reactions without a change in charge, and to systems with multiple reactions, e.g. acid-base titrations.

We have shown that UV-vis spectroscopy is well-suited for measuring chemical equilibria in SCW. A simple stopped-flow apparatus with a 200  $\mu\text{L}$  optical cell was developed and used up to 450 C and 400 bar(Bennett, 1994; Xiang, 1994). The solution may be replenished in 30 s to prevent buildup of impurities and to change solution composition rapidly. By stopping the flow, more precise spectra may be obtained. The ability to obtain spectra rapidly is especially important in alkaline solutions, e.g. 0.05 m KOH, as corrosion of the sapphire windows becomes noticable in minutes. A 2.54 cm od by 0.476 cm id Inconel 625, titanium (grade 2) or stainless steel cylindrical spectroscopic cell with a path length of 1 cm contained two 0.953 cm diameter by 0.476 cm thick sapphire windows sealed with 0.025 mm thick gold foil on the inside surface. The disposable windows were sealed without introducing crevices that would otherwise trap impurities and lead to long mixing times. The reference beam was masked with the same aperture as the sample. Window failure due to differences in thermal expansion of sapphire and stainless steel was relatively common above 350 C, but less common for the Inconel 625 cell and rare for titanium cell.

Substantial progress has been made on developing a series of four pH indicators for supercritical water (SCW) solutions over a wide range of acidity(Johnston & Chlistunoff, 1998; Ryan, Xiang, Johnston, & Fox, 1997; Wofford, Gloyna, & Johnston, 1998; Xiang & Johnston, 1994; Xiang & Johnston, 1997; Xiang, Johnston, Wofford, & Gloyna, 1996). To our knowledge, these were the first quantitative measurements that have been made of pH in supercritical water. We used these indicators to measure the pH of unknown solutions and to perform acid-base titrations between sulfuric acid and ammonia, KOH and acetic acid, ammonia and acetic acid, HCl and NaCl, HCl and KOH and boric acid-borate solutions and HCl. An important result was that sodium borate neutralizes HCl very effectively at 350°C. The ability to neutralize acids in hydrothermal oxidation to control corrosion and manipulate salt recovery is one of the key issues in the technology.

From UV-vis spectroscopic measurements and molecular dynamics simulation of chemical equilibria, we have shown that density effects on reactions may be explained in terms of changes in charge dispersal between the relevant chemical states. From the simulations, the thermodynamic solvent effects has been explained in terms of the local structure of water about the reacting species. The synergism from combining

spectroscopy and simulation has provided a great deal of understanding into chemical thermodynamics and dynamics in supercritical water.(Johnston et al., 1998)

### **Absorbance spectroscopy of chemical equilibria in supercritical water without the use of pH indicators**

For systems with chromophores such as Cr(VI), UV-vis spectroscopy may be used to study chemical equilibria directly without a pH indicator. The chemical equilibria of Cr(VI), which are of interest in corrosion in hydrothermal oxidation, were studied directly by UV-Vis spectroscopy (280 to 500 nm) to 420 °C.(Chlistunoff & Johnston, 1998) A new system made completely of titanium with gold foil seals and sapphire windows was sufficiently resistant to corrosion that high quality spectra could be obtained. The previous literature data on the acid-base equilibria of Cr(VI) were limited to temperatures not exceeding 175 °C. The dissociation constants of  $\text{H}_2\text{CrO}_4$  ( $K_{a1}$ ) and  $\text{HCrO}_4^-$  ( $K_{a2}$ ) were measured in acid and alkaline solutions with perchloric acid and KOH. The predominant Cr(VI) species in alkaline (KOH) solutions at elevated temperatures are chromate ( $\text{CrO}_4^{2-}$ ), bichromate ( $\text{HCrO}_4^-$ ), and at temperatures above 260 °C,  $(\text{K}^+)(\text{CrO}_4^{2-})$  ion pairs become prevalent. For fixed Cr(VI) and KOH concentrations, the molal concentration of  $\text{HCrO}_4^-$  initially increases with temperature but decreases again in the vicinity of water's critical point where the density decreases substantially. The decrease in  $\text{HCrO}_4^-$  at high temperature and low density may be attributed to  $(\text{K}^+)(\text{CrO}_4^{2-})$  ion pairs, to a high degree of electrostriction about  $\text{CrO}_4^{2-}$ , which facilitates the reaction  $\text{HCrO}_4^- + \text{OH}^- = \text{CrO}_4^{2-} + \text{H}_2\text{O}$ , and to ion activity coefficients.

In a second project, UV-Vis spectra of aqueous  $\text{HNO}_3$  solutions were measured up to 400 °C(Chlistunoff et al., 1998). It was found that  $\text{HNO}_3$  decomposes above 300 °C to form  $\text{NO}_2$ ,  $\text{HNO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$  (in presence of  $\text{NaNO}_2$ ) and oxygen. The spectra were manipulated by adding  $\text{NaOH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NaNO}_2$  or mixtures of these compounds to  $\text{HNO}_3$  solutions. Individual bands corresponding to  $\text{HNO}_2$  and  $\text{NO}_2$  could be determined using numerical deconvolution of the spectra. Areas of the deconvoluted bands were fitted numerically to determine optimal values of the extinction coefficients of  $\text{NO}_2$  and equilibrium constants for the reactions:  $\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$ ;  $2 \text{HNO}_3 = \text{H}_2\text{O} + 2 \text{NO}_2 + 1/2 \text{O}_2$ ;  $2 \text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$ ;  $2 \text{HNO}_2 = \text{H}_2\text{O} + 2 \text{NO} + 1/2 \text{O}_2$ ;  $2 \text{NO} = \text{N}_2\text{O} + 1/2 \text{O}_2$ ; and  $\text{Na}^+ + \text{NO}_3^- = (\text{Na}^+)(\text{NO}_3^-)$

### **Molecular Dynamics Simulations of Reactions in Supercritical Water**

The first molecular dynamics computer simulations of SCW solutions considered the structure of water molecules about various solutes. Our contribution has been to determine free energies of reactions and ion solvation in SCW and to relate these results to the solution structure to provide a complete molecular description. We have performed the first simulations to determine the free energy of solvation of ions in SCW including  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{HCl}$ , and  $\text{H}_2\text{O}$ (Balbuena, Johnston, & Rossky, 1996a; Flanagan, Balbuena, Johnston, & Rossky, 1997). We have also pioneered the simulation of free energy barriers for reactions in supercritical fluids, in particular electron transfer(Balbuena, Johnston, & Rossky, 1994; Balbuena, Johnston, & Rossky, 1995; Flanagan, Balbuena, Johnston, & Rossky, 1995) and acid-base reactions(Balbuena, Johnston, & Rossky, 1996b) and have utilized these results to develop continuum models(Bennett, Rossky, & Johnston, 1995; Flanagan, et al., 1997). We have also simulated dynamic properties of ions in supercritical water with molecular dynamics techniques.(Balbuena, Johnston, Rossky, & Hyun, 1998) Our objective has been to calculate friction coefficients of ions in aqueous solutions at infinite dilution with a semi-continuum hydrodynamic model. The molecular part of the model



utilizes MD simulation to incorporate local friction present in the first coordination shell. The local friction is expressed in terms of the rotational reorientation times for water about a central water molecule and about a central ion. One expects that this time is correlated with the degree to which the ionic motion can be described as diffusion of the ion and its hydration shell as a unit, or in the other extreme, diffusion of the bare ion in bulk solvent. A number of important conclusions of this study are given in the paper of Balbuena et al. (1998).

As noted in the experimental work (Green, Xiang, Johnston, & Fox, 1995; Ryan, Xiang, Johnston, & Fox, 1996; Ryan, et al., 1997) throughout this project, the role of local density augmentation in influencing chemistry in supercritical fluids, and SCW in particular, is a key element to our understanding of experimental data. While such data can be interpreted effectively based on such a conceptual basis, and simplified model descriptions of the underlying molecular effects can be used to provide a quantitative aspect to this interpretation, it is difficult to quantitatively infer molecular details from experiment alone, at least at this stage of development. Spectroscopic data reports on the local environment only indirectly, although, as demonstrated by the discussion above, very valuably. New experimental results coming from the area of neutron scattering, in particular, are providing new direct probes of structure in both pure SCW and solutions, and promise to change this situation significantly. However, the neutron scattering approach remains limited by both challenges in data analysis and limits on solute concentration.

Computer simulation studies, using models based at the level of intermolecular potentials and employing rigorous statistical mechanical protocols, now have a substantial history demonstrating their usefulness for the generation of reliable and molecularly detailed views of condensed phase structure and dynamics. Since experiments in SCW are difficult, simulation is a particularly important route of investigation. From such calculations, one can obtain not only those quantities that are in principle measurable, but more importantly, a microscopic view of the system that can provide a more detailed conceptual framework for interpreting and directing further experiment. At the same time, simulated solution structure and dynamics provides an ideal guide for the development and testing of more simplified, computationally facile models that can be readily implemented by both theorists and experimentalists. The use of simulation as a means of testing the validity of more simplified models, such as those involving a continuum solvent description, is one of the goals of the work described here, as discussed below.

In this section on simulation, we first outline some key elements of the methodology used to carry out the simulations and their analysis. We comment specifically on the models used for the solvent, an area in which there has been considerable controversy. We then describe some of the derived results relating to single ion solvation structure and free energy, and the character of local density augmentation in this context. The reflection of this in activation free energies for ionic reactions and for acid-base equilibria, in particular, is then discussed.

#### *Methods*

The elements of computer simulation are very well established and therefore we do not repeat these here. All of our work has employed MD sampling.

The solution of interest is necessarily modeled using a finite system containing typically several hundred molecules of solvent. The infinite system is mimicked by the use of periodic boundary conditions which reproduce the primary cell periodically in space to produce an infinite system. Although for some quantities, a truncation of the potential at a distance of  $\sim 10$  Å between interacting molecules is sufficiently accurate, and it is in this manner that we carried out some of our earliest simulations, it is preferable for systems with long ranged electrostatic forces to sum all long ranged interactions without truncation. It is noteworthy that dynamical quantities, such as ionic diffusion constants, have been shown to be particularly susceptible to artifacts associated with potential truncation.

The models used in our own work are of the interaction site type, where the intermolecular interactions result from a sum over pairwise interactions among sites in each molecule. Typically, each atom of the system is associated with a short ranged potential consisting of a Lennard-Jones 6-12 form, describing molecular shape and dispersion effects, and separately a partial charge describing a contribution to the electrostatic interactions. Such models dominate the descriptions used successfully for systems as diverse as CO<sub>2</sub> and biopolymers.

It is worth briefly discussing the models for pure water that are used in our work. In the work described here, the water model SPC (simple point charge), and its slightly reparameterized version SPC/E, consist of a single Lennard-Jones sphere centered on the oxygen nucleus and three point partial charges, located at the two hydrogen nuclei (charge  $\sim +0.4e$ , where  $e$  is the magnitude of the charge of the electron) and oxygen nuclei (charge  $\sim -0.8e$ ). The molecular HOH bond angle is constrained at the ideal tetrahedral angle. The pure solvent thermodynamics, including coexistence curve location, critical parameters, and dielectric constant are, in fact, rather well reproduced by the SPC models, and SPC/E in particular. Further, when the SPC/E model is applied to SCW, the calculated structural results agree with recent experimental neutron scattering data approximately as well in SCW as in ambient water. Separate recent experimental tests from laboratories at Saclay show that the angle resolved scattering appears to be within the uncertainty of the comparison.

It is striking that SPC models do so well in SCW. The successes of the model are not limited to these respects. It has been shown previously that under near ambient conditions, the SPC model reproduces essentially quantitatively the temperature dependence of the measured X-ray scattering amplitude, as well as the isotope (H<sub>2</sub>O  $\leftrightarrow$  D<sub>2</sub>O) dependence of this scattering. The latter is a purely quantum effect. Hence, the SPC models have shown themselves to be remarkably robust caricatures of fluid water, and well supported for our studies of SCW.

The calculation of solvation free energies plays a central role in the present context, as well as in many others. Computationally effective means to access this important quantity have been developed and widely applied, particularly within the area of biophysical simulation. The key formal relation is

$$\Delta A = -k_B T \ln \langle \exp [-\Delta U/k_B T] \rangle_{U_{\text{ref}}} \quad (1)$$

where

$$\Delta U = U - U_{\text{ref}}; \Delta A = A - A_{\text{ref}}$$

$k_B$  is Boltzmann's constant,  $T$  is the temperature, and the subscripted bracket denotes an equilibrium average over configurations of an ensemble governed by the potential energy function  $U_{\text{ref}}$ . Here,  $U$  is the potential energy function for the system with Helmholtz free energy  $A$  and  $U_{\text{ref}}$  is the potential energy function for the system with free energy  $A_{\text{ref}}$ . This *exact* result is given here for constant volume and temperature (canonical ensemble), but corresponding expressions for constant pressure are also readily obtained. In order to compare to experiment, one route is to convert the results obtained in one case to that in the other via thermodynamic results involving macroscopic properties such as the compressibility.

By a suitable choice of end point potential functions in applications, the result given in Eq. (1) can be used, for example, to calculate the free energy difference between a system of pure solvent and one with insertion of a solute or to calculate the difference in solvation free energy for a pair of solutes. Practically, in order to obtain accurate results, the creation of, or "mutation" among, chemical species must be done in steps which gradually change the potential between endpoints describing the initial and final states, as described elsewhere. The total free energy change is then obtained simply by adding the free energy increments obtained at each partial step. The approach has been found to be a reliable and numerically well behaved one and so is very effective.

In certain contexts, the calculation of free energy differences is difficult to access computationally (Balbuena, et al., 1996b). Examples would include problems in which

a large amount of solvent would need to be displaced in a chemical association, one in which a large conformational change occurs, or one in which a complex chemical intermediate is present. In these cases, one of which is described below in the context of acid-base chemistry, the method can often be readily combined with a hypothetical free energy cycle, with individual legs that are each readily evaluated computationally as discussed below.

As noted above, the use of a continuum solvent model is one of the most appealing ways to describe solvation in a readily tractable form, and one we will consider further below. We note here that for spherical geometries (spherical solutes) with uniform solvent density, the description is simply given by the Born equation. In general, for nonuniform dielectrics and nonspherical solute geometries, the underlying Poisson equation can be solved numerically (Bennett, et al., 1995). For non-uniform solvent density and spherical solutes, the equations can also be readily solved, in many cases analytically. More generally, the numerical implementation of this approach for arbitrary molecular solutes in a uniform solvent has been carried out conveniently in the program DELPHI, a methodology which is very widely used for macromolecular solutes in the biophysical community. Generalization to the case of an arbitrary nonuniform density which is found self-consistently based on the bulk equations of electrostriction has been carried out by Tucker and coworkers, extending the spherical solute theory of Wood and coworkers.

#### *Ion solvation and local density augmentation*

For highly polar and ionic solutes, it is easy to anticipate local density augmentation in the solute vicinity. A characteristic temperature for near neighbor water-water interactions, defined as the ratio of the typical interaction energy divided by  $k_B$  is of the order of 1000K, while that between a univalent ion and water is of the order of 5000K. Thus, one must expect that at typical temperatures in SCW, considerable attractive water-water interactions persist and that ion-water interactions will dominate those among water molecules. The questions of interest in a simulation are the magnitude of the local solvent density augmentation near the solute, the spatial range of such enhancement, and the degree to which such enhancement persists with decreasing solvent bulk density and increasing temperature. These last characteristics are those that determine the degree to which entropy can overwhelm the simple energetic preferences.

In Fig. 1, we show examples of simulated radial density profiles for solvent centers around a single dilute chloride ion at the indicated supercritical and ambient water (AW) conditions. (Flanagan, et al., 1995) In these cases, the density and temperature ( $\rho_r$ ,  $T_r$ ) of SCW is indicated in units reduced by the critical values for SPC/E water (0.29 g/cc, 640K). As is evident in the figure, although the density in the immediate neighborhood of the ion is reduced from ambient conditions, it is far higher than the bulk density and notably insensitive to variation in both temperature and bulk density at these SCW states. Further, the large density enhancement is largely limited to a single solvation shell. Only when the density decreases or temperature increases dramatically ( $\rho_r \sim 0.1$  or  $T_r \sim 1.3$ ), does one see significant variation. This is in contrast to polar molecules with solute-solvent interaction energies comparable to water-water, such as HCl, where the enhancement is both smaller and much more responsive to bulk conditions. An examination of the interaction energy distributions in these ionic solutions show a corresponding level of insensitivity to bulk solvent density and to temperature.

These observations suggest that ionic hydration under these conditions might be described well by an adsorption model (Flanagan, et al., 1997), which can be tested directly using simulation data. If one defines a local solvent density  $\rho_{loc}$  by the average simulated density over the first solvent shell, then for an adsorption equilibrium, characterized by a constant  $K$ , between the bulk density  $\rho$  and the first shell leads to the relation

$$\frac{\rho}{\rho_{loc}} = \frac{K}{\rho_{max}} + \frac{\rho}{\rho_{max}} \quad (2)$$

where  $\rho_{max}$  is the saturation density in the first solvation shell. A representative example of the appropriate plot (Fig. 2) shows that the model works extremely well. In addition, it is evident that the intercept, determining  $K$ , is quite small. Thus, in accord with this insensitivity, the approximation that  $\rho_{loc} = \rho_{max}$  is very effective, and one finds further that  $\rho_{max}$  is well correlated with simply the ionic surface electrostatic potential, or the charge/radius ratio of the ion.

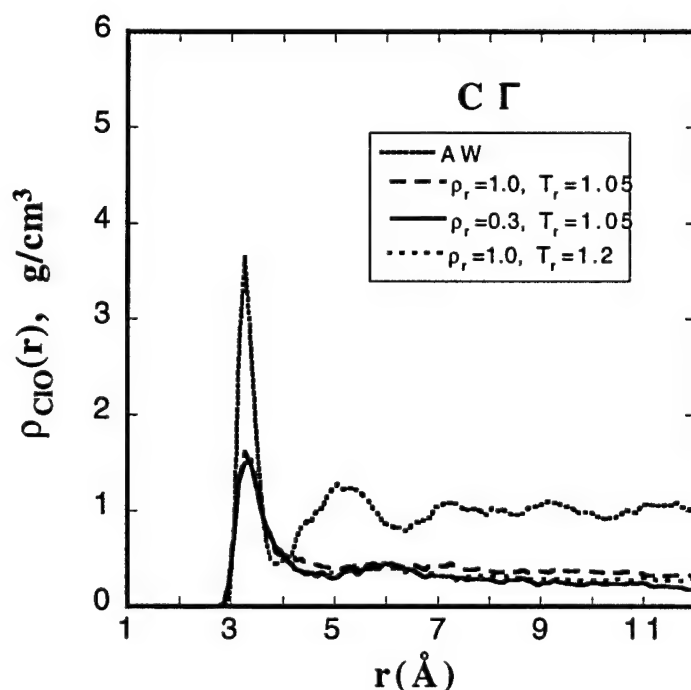


Figure 1 Spherically averaged site-site solute-water local density distribution functions for  $\text{OCl}^-$  in AW and SCW

One can push this model a bit further and ask if the simple single shell model using the average first shell densities captures the solvation thermodynamics as well. In Fig. 3, we show the comparison of simulated  $\text{Cl}^-$  hydration free energies with those obtained from a concentric shell continuum dielectric solvent model (Johnston, Bennett, Balbuena, & Rossy, 1996). Here, the first shell is described by a region of enhanced dielectric constant  $\epsilon$ , determined via bulk  $\epsilon(p)$ , while the entire remainder of the fluid is set to the uniform bulk  $\epsilon$  at the conditions of interest. From the figure, it is

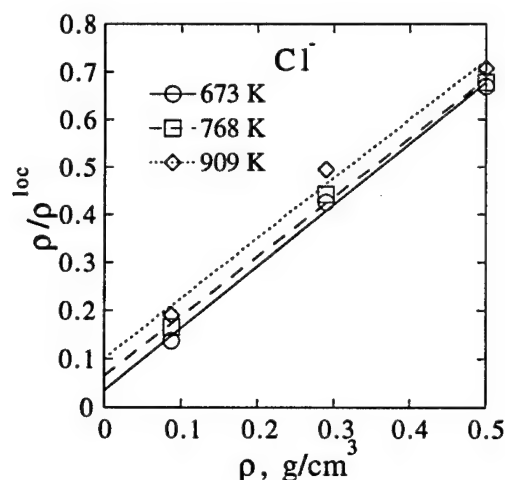


Figure 2 Linearized Langmuir isotherms for the local density of water about the  $\text{Cl}^-$  ion

evident that the simple model does a good job of capturing the thermodynamic consequences of the density enhancement. Of note in Fig. 3 is the apparent inflection in simulated isotherms with decreasing density (e.g.,  $T_r = 1.05$ ), and the clear lack of single valued behavior when the data are plotted against a conventional Born like parameter ( $1 - 1/\epsilon$ ). It is also worth pointing out that the straight line behavior characteristic of the Born theory (see Fig. 3) pertains best at the higher densities and highest temperatures, and not at lower densities, as a result of the adsorption behavior.

The effect of this adsorption phenomenon can be seen, for example in the activation free energy of a simple chemical reaction, the symmetric  $\text{S}_{\text{N}}2$  reaction of  $\text{Cl}^-$  with  $\text{CH}_3\text{Cl}$  in SCW. This reaction has been studied in great detail in ambient conditions as well as in supercritical water.(Flanagin, et al., 1995) Concisely, we note here that the large solvent induced barrier to reaction that follows from the delocalization of charge, and correspondingly lower magnitude of solvation free energy at the transition state is found to be relatively weakly responsive to the solvent thermodynamic state. In fact, at relatively high solvent densities ( $\rho_r \sim 2$ ), the values are quite similar to those at ambient conditions and are well reproduced by the result of a free energy calculation using a uniform, bulk, solvent density. At lower density the activation free energies are notably overestimated by this continuum model, a result of the relatively improved solvation of the charge localized reactant ion compared to the transition state. Nevertheless, the dominant effect that would influence reaction rates in comparison to ambient conditions is found to be simply the temperature, not the solvation characteristics and free energies. It is notable that a compressible, nonuniform, continuum solvent model of Tucker underestimates the first shell local density significantly, but does produce sufficient density (and thus dielectric constant) enhancement to reproduce simulated free energies quite well.

With this understanding, we now turn to acid-base chemistry. Acid-base equilibria are determined by a combination of large intramolecular bond energies, characteristic of the gas phase solutes, and large solvation free energies, leading to a delicate balance. To understand such reactions in more detail, we have carried out simulations related to the reactions(Balbuena, et al., 1996b)



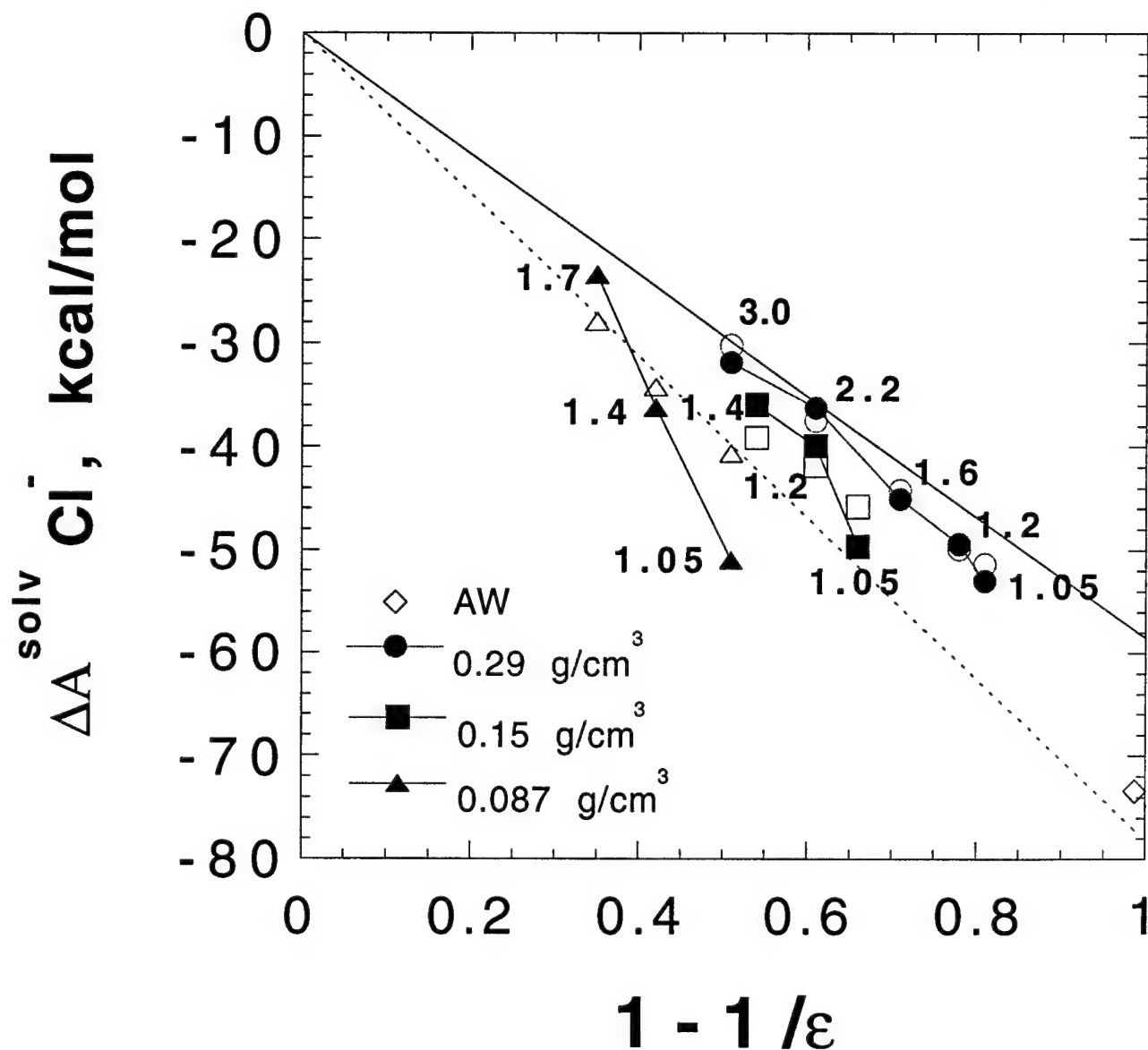


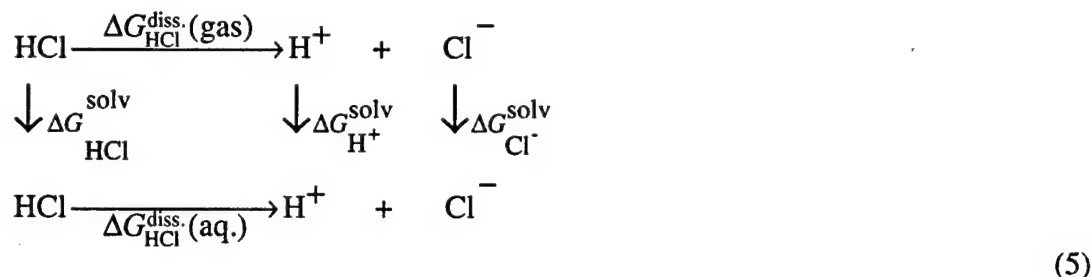
Fig. 3 Comparison of the continuum electrostatics Born model (ion radius: 2.128 Å, dashed line; 2.8 Å, solid line); modified continuum model (open symbols) and MD simulation (filled symbols connected by lines) for the free energy of solvation of the chloride ion from ambient to supercritical conditions. (The point labels represent temperatures reduced with respect to  $T_c$  of the model, 640K)



Since a modeling method for  $H^+$  is not well established, as a result of the need to include chemical interactions with the solvent and possibly quantum effects, it is far more effective to look at the *difference* between these reactions. The corresponding proton transfer reaction



can be studied via the free energy methods indicated earlier when supplemented by the cycle



In this case, it is not hard to see that the *difference* between the free energies characterizing the two acid dissociation reactions above in Eq. (3) corresponds to the free energy difference of Eq. (4). Computationally (or experimentally), one needs to compute

$$\begin{aligned} \Delta G_{HCl}^{diss.}(aq, T, P) - \Delta G_{HOH}^{diss.}(aq, T, P) &= 2.3RT(pK_a - pK_w) = \\ &= [\Delta G_{HCl}^{diss.}(gas, T, P \rightarrow 0) - \Delta G_{HOH}^{diss.}(gas, T, P \rightarrow 0)] + \\ &+ [\Delta G_{Cl^-}^{solv} - \Delta G_{OH^-}^{solv}] - [\Delta G_{HCl}^{solv} - \Delta G_{HOH}^{solv}] \end{aligned} \quad (6)$$

which can be seen to be the difference in gas phase dissociation energies plus the difference in solvation free energies of the neutrals and the difference in solvation free energies of the ions.

Reanalysis of the available experimental data for these reactions leads to the conclusion that the free energy associated with the proton transfer in ambient up through SCW is remarkably very nearly a constant as a function of temperature, if the density is held constant above the critical point. To understand this, we have combined gas phase dissociation energies with simulated solvation free energy differences for each neutral species pair and ionic species pair. The results of those simulations and of a uniform continuum solvent model calculation via Poisson's equation are shown in Fig. 4(Bennett, et al., 1995). As can be seen in this figure, the first obvious origin for the noted near constancy of  $\Delta\Delta A$  is that the difference free energies are not strongly sensitive to dielectric constant, a result which is reasonable for these pairs of similar species. Further, the contribution from ions and neutrals tend to cancel each other. Thus, the net free energy change is dominated by the constant gas phase term, with only a relatively weakly varying solvent contribution.

In addition, in light of the emphasis placed on solvent clustering, it may seem surprising at first that the uniform solvent model is evidently highly successful. The origin of this fact is again cancellation for similar reactant and product species. If the reaction in Eq. (4) were not isocoulombic, one would certainly obtain a very different result. Given that the simplest continuum model has been demonstrated via molecular simulation to be successful, we can then use it to map the proton transfer free energy as a function of thermodynamic state, as shown in Fig. 5(Bennett, et al., 1995). It is evident that the constant solvent density free energy difference is indeed very nearly constant, and also continuous, from near ambient through supercritical regions, in accord with experiment. On the other hand, the isobaric values show significant deviations from this

constancy above the critical temperature due to rapid variation in the dielectric constant with density, reflecting the dependence that is manifested in Fig. 4.

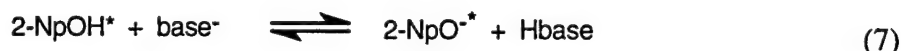
It is notable that the behavior of the quantitative values of the free energies that we have analyzed at a molecular level here mimic the rates of the isocoulombic proton transfer (and thus activation free energies) discussed above. The principles governing both are seen to be the same, and thus a deeper understanding of both proton transfer equilibria and kinetics results from the combination of theory and experiment.

### Fluorescence Spectroscopy and Reaction Dynamics in Supercritical Water

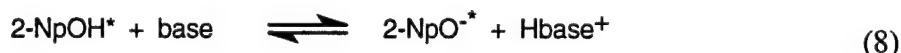
Our ultimate aim is the ability to tune fluid pressure and temperature to optimize a desired outcome in chemical kinetics. We have studied how solvent-solute interactions and molecular-scale processes can influence the kinetics of proton transfer reactions in SCW. The first studies examined a classic system 2-naphthol, and the second system was acridine.

The results for the excited-state deprotonation of 2-naphthol provided important fundamental information about proton transfer to water versus proton transfer to a borate buffer. The experiments were limited to subcritical conditions. Time-resolved data were collected by single-photon counting at the Center for Fast Kinetics Research in the nanosecond time frame. To our knowledge, this is the first time fast kinetics have been studied in SCW.

Proton transfer reactions from  $\beta$ -naphthol to several bases were studied in subcritical and supercritical water up to 400°C. The isobaric rates of excited-state deprotonations of 2-naphthol by acetate and borate anions exhibit only modest deviations from linear Arrhenius behavior from ambient temperature to nearly the critical temperature of water

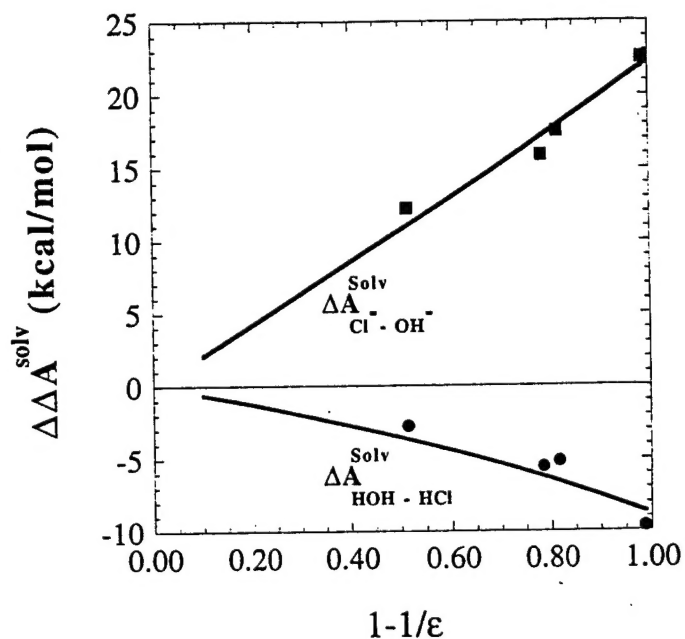


In contrast, the rates of deprotonation by ammonia and water exhibit marked deviations from Arrhenius-like behavior and go through a maximum at high temperatures:

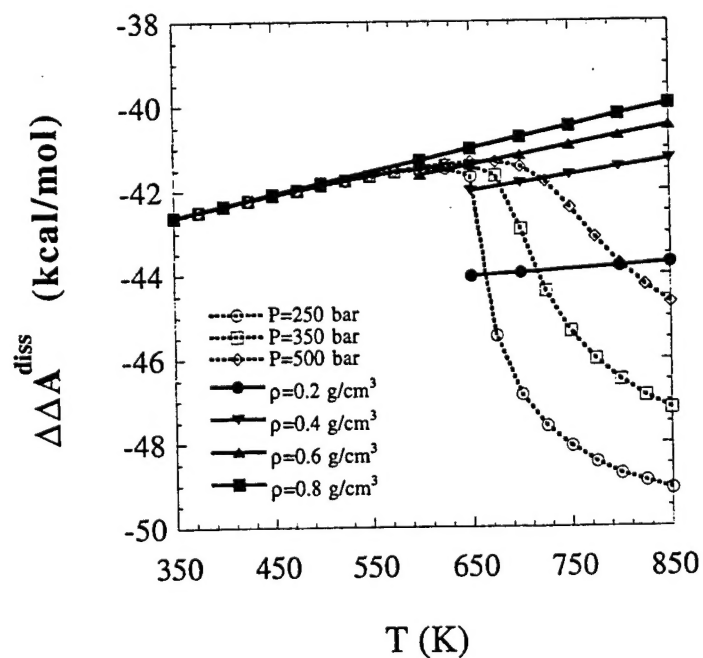


These observations establish a fundamental difference in how the rates of charge-generating reactions, such as proton transfers to neutral molecules like ammonia and water, and those in which ionicity is unchanged (isocoulombic), such as proton transfers to acetate and borate anions, depend on temperature. The loss of local water structure, hydrogen bond interactions, and changes in dielectric constant with temperature have a much more profound influence on the charge-generating reactions. These results were interpreted using transition state theory and compared with several molecular dynamics - free energy perturbation simulations.

To investigate proton transfer, the isobaric acid/base equilibrium between acridine and the acridinium cation was measured from ambient temperature to 380 °C (above the critical temperature of water,  $T_c = 374$  °C) using absorption spectroscopy. (Ryan, et al., 1997) At 3500 psia, the isobaric protonation of acridine is shown to be exothermic up to approximately 315 °C. Above 315 °C, protonation becomes endothermic due to changes in the dielectric constant of water with temperature which have a profound influence on the solvation of ions. The results have been interpreted using a modified Born equation to account for the temperature dependent changes in acridinium cation and proton solvation. The absorption and fluorescence spectra and the fluorescence lifetime of acridine are sensitive to changes in solvent-solute hydrogen bonding. Hydrogen bonding between acridine and water is observed to decrease from ambient temperature to the



**Figure 4** Relative solvation free energies of the ionic and neutral species (parameters of Table 1) that appear in the reaction  $\text{HCl} + \text{OH}^- = \text{Cl}^- + \text{H}_2\text{O}$  (lines: standard continuum model, symbols: MD simulation ).



**Figure 5** Relative free energy of dissociation of hydrogen chloride versus water along various isochores and isobars from the standard continuum model.

critical temperature. A relatively rapid change in hydrogen bonding occurs between 100 and 200 °C.

### **Pulse Radiolysis in Supercritical Water**

In the following two recent studies, pulse radiolysis techniques have been used as a route for activating solutes in SCW. In this technique, high energy electrons bombard a solution inducing ionization of solvent and, upon equilibration, solute. By electron attachment, the corresponding solute radical anions and their fragmentation products can also be observed. The hydroxy radical is a primary radiation product in water. Its subsequent chemical reactivity has been monitored by optical methods to understand how the structure of SCW influences reaction dynamics.

#### ***Effect of Temperature on the Reaction of HO• with Benzene and Pentahalogenated Phenolate Anions in Subcritical and Supercritical Water***

The dioxygen-mediated oxidation of organic compounds in subcritical and supercritical water ( $T_c = 374.2\text{ °C}$ ,  $P_c = 3160\text{ psia}$ ) is thought to involve the intermediacy of hydroxyl (HO•) and hydroperoxyl (HOO•) radicals. This assumption is based on the products resulting from the partial oxidation of several different families of organic compounds. In this study, the decay kinetics of the transient phenoxyl and HCH radicals derived from the HO•-mediated oxidation of aqueous pentabromophenolate, pentachlorophenolate, and pentafluorophenolate anions and of benzene are used to probe the effects of temperature on the initial oxidations of these compounds in subcritical and supercritical water. (Ferry and Fox, 1998)

The pulse radiolysis experiments were performed with a 4 MeV van de Graff accelerator, with a pulse width of 1000 ns. Transient absorptions were measured using a 250 W Xenon lamp, grating monochromator, and photomultiplier arrangement, as described earlier. Aqueous KSCN (0.080M) was used for dosimetry. The time dependence of the absorption spectra were recorded on a Biomation 8100 digitizer interface interfaced with an Acer 386SX PC for data analysis.

Pulse radiolysis was carried out in a Ti (grade 2) flow-through cell fitted with sapphire windows for optical monitoring. The electron beam passed through a Ti "window", a solid plug of Ti inserted into the cell with drilled thin spots analogous to previously described steel electron beam windows. The total volume of the cell was 300  $\mu\text{L}$ . The following conclusions were found in this study. The yields of the HO• adducts produced by HO• addition to benzene, pentabromophenolate, and pentachlorophenolate decreased in increasing temperature, whereas the yields of the corresponding phenoxyl radical seemed constant. This observation indicates that the mechanism by which the HO• adducts decay at high temperature did not involve the loss of hydroxide ion to generate the corresponding phenoxyl radical. Instead, a coupling mechanism may have been more important. Although the local structure of the solvent around the solute may have influenced the decay kinetics of HCH and the pentabromophenoxyl radical, it did not have any apparent effect on the product distribution. Rather, in all cases where it was possible to differentiate between products, temperature seemed to be the most successful predictor of product distribution.

#### ***Kinetics of Carbonate Radical Reactions***

Pulse radiolysis was used to generate the carbonate radical ( $\text{CO}_3^{\cdot-}$ ) in subcritical and supercritical water. The effect of the charge on the reaction partner of aqueous carbonate radical reactions was examined over the temperature range 30°C–400°C, at 4150  $\pm$  75 psia, pH 10.55. The rate constant for oxide transfer between two  $\text{CO}_3^{\cdot-}$  was insensitive to temperature below 200°C, but increased from  $1.61 \times 10^7\text{ M}^{-1}\text{ s}^{-1}$  to  $2.90 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$  between 200°C and 400°C, increasing by a factor of 300. The rate constants for the one-electron oxidation of aniline, *p*-aminobenzoate, *N,N*-dimethylaniline and *p*-*N,N*-dimethylaminobenzoate by  $\text{CO}_3^{\cdot-}$  were determined under the same conditions. All displayed a negative temperature dependence at temperatures below 320°C. Above

320°C, the rate constants for the oxidation of the anionic aminobenzoates by  $\text{CO}_3^{3-}$  increased sharply, whereas those for the oxidations of the corresponding neutral anilines did not increase until 360°C.

### Electrochemical Reactions in Supercritical Water

The main progress during the period covered by the current project was related to the cell assembly. We proved that cells constructed with oxidized titanium parts are generally applicable for both supercritical systems as well as electrochemical cells. The corrosion of the titanium cell is negligible if the solution is free of halide and reduced by orders of magnitude over stainless steel in the presence of chloride. However, the titanium parts need reoxidation in case of mechanical damage of the protecting oxide layer. Application of titanium tubes also helps to avoid fragility and danger of explosion, which was the main danger for alumina tubes.

The problem of the electrical insulation of the electrodes of different function was also solved. Composite Graphite-Vespel ferrules (produced for HPLC systems) are sufficient to hold and insulate the electrodes and other parts connected to the cell in acidic solutions, provided the connection is made far from the hot zone and the ferrules themselves are not exposed to temperatures higher than 250 °C. In this case, the chemical contamination caused by the ferrules is also negligible.

The electrode metal insulation with glass is of great importance in scientific work, allowing the preparation of microelectrodes. It was found that widely used Pyrex 7710 glass is unsuitable for electrode fabrication due to corrosion, mismatch in thermal expansion with most metals and increased conductivity at high temperature. Glasses with high  $\text{PbO}$  content were sufficient, especially Corning 8870. This glass fulfills most requirements, but its corrosion results in the presence of corrosion products in the outflow (lead and antimony).

Several chemical systems were studied by means of the experimental device described above. Voltammograms were recorded, diffusion coefficients and particle sizes were calculated. We found that the temperature dependence of the diffusion of several particles obey the Stokes-Einstein relationship, and the exceptions can be explained with decomposition. Thermodynamic data were calculated for the  $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}$  system. A paper describing this research is being prepared.

The electrode sealing materials (especially Corning 8870 glass) were investigated in order to identify any corrosion products. It was found that most components have no impact on the electrode behavior, although XPS results show that the glass is etched in high temperature aqueous media. During the etching, the surface layer to the depth of several nanometers is depleted in the glass constituents other than  $\text{SiO}_2$ . Only antimony was identified as a component that interferes with the electrochemical processes. Antimony(III) oxide is an additive to the glass in 0.1-0.5%; however, it can be adsorbed on the electrode metal, which results in the appearance of an anodic peak while oxidized to antimony(V). Due to the harmful effect of the antimony(III), like oxide formation in a few monolayer thicknesses and the corresponding oxide reduction, it was not possible to carry out an investigation of surface peaks with the accuracy required. Several methods were tested for electrode preconditioning in order to prevent the antimony(III) emission at high temperature, including etching at 100°C in dichromate, peroxide or bromine solutions, but none of them were suitable to prevent the glass etching at higher temperatures.

Electrochemical behavior of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) was investigated in 0.2 M  $\text{NaHSO}_4$  supporting electrolyte. It was revealed that solutions made at room temperature unavoidably contained  $\text{TMPD}^+$ . TMPD is oxidized in a 2-electron process at low temperature, but two independent processes can be observed at temperatures higher than 120°C. This wave splitting is merely due to the change in the pH of the solution employed, that can also be achieved at room temperature by modifying the supporting electrolyte. Decomposition was observed at temperatures higher than 280 °C, and data could not be analyzed quantitatively. The diffusion coefficient of TMPD follows the Stokes-Einstein relationship in the temperature range of stability.

Investigation of oxalic acid solutions at high temperature enabled us to follow the spontaneous decomposition of oxalic acid and investigate the electrochemical behavior of carbon monoxide beyond 220°C. The effective radius of the diffusing particle as calculated with the help of the Stokes-Einstein equation is 3.8 nanometer for the oxalic acid stock solution at room temperature; this decreases down to about 1.9 nanometer at 250°C. Comparison with CV-s recorded for formic acid led us to the conclusion that the decomposition product is CO only. Another drop in the calculated particle size was observed at 340°C, which cannot be correlated to any chemical change or bond length. We believe it is due to the change in the mechanism of the diffusion of CO in the vicinity of the critical point. The kinetics of the decomposition of oxalic acid were also investigated. We found that the rate constants published in the literature were applicable to calculate the decomposition rate of oxalate in our experimental setup.